

Difficulties of technogenic formations roasting products processing into the portland cement clinker in the presence of a significant amount of SO₃

Oleg Sheshukov^{1,2,} and Egiazaryan Denis^{1,2}*

¹ Federal State Budgetary Institution of Science Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, 620016, Ekaterinburg, Amundsen st., 10, Russia

² Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N.Yeltsin», 620002, Ekaterinburg, Mira st., 19, Russia

Abstract. Synthesis of the portland cement clinker in the presence of a significant amount of SO₃ is difficult due to the tricalcium silicate formation suppression. Since some technogenic formations contain a significant amount of SO₃ it is hard to obtain the portland cement clinker from it. The analysis of the SO₃ influence on the clinker-formation thermodynamic process allowed to reveal a number of regularities of their occurrence and to propose a method for the raw mix composition calculating and its preparation to ensure a stable portland cement clinker synthesis.

Some technogenic formations, for example, sludge from the synthetic fibers production, contain zinc in sulphide form. The feature of the such sludge phase composition is the iron oxides lack in them and the gypsum dihydrate presence. A significant amount of gypsum-anhydrite remains in the roasting products after zinc extraction from such sludge. Table 1 shows the phase composition of the sludge roasting products obtained at the temperature of 1100 °C.

To ensure integrated waste-free processing of synthetic fibers production, it is advisable to convert the roasted products after complete extraction of zinc sulfide into portland cement clinker, but the gypsum-anhydrite presence makes it difficult to implement this sludge complex processing direction.

It is well known from the practice of portland cement production that it is difficult to obtain high-quality portland cement clinker from a raw material mixture with a significant amount of gypsum-anhydrite, which is a source of SO₃. According to [1, 2], with an increase in the SO₃ in the raw mixture, the amount of dicalcium silicate (C₂S) increases, tricalcium silicate (C₃S) decreases, and with an equal total content of these phases in the clinker, their C₃S/C₂S ratio decreases. Since C₃S is the most active and refractory component, decrease in its content leads to a decrease in refractoriness and activity of clinker. It was found [3] that with an increase in the content of SO₃ in portland cement

* Corresponding author: silast@mail.ru

clinker, also the tricalcium aluminate (C_3A) content decreases. According to the authors, the reason for the C_3A content decrease in high-sulfate clinker is the silicon isomorphous replacement in silicate phases with aluminum. The reasons for the C_3S content decrease in portland cement clinker with an SO_3 content increase in it was not found in literary sources.

Table 1. The phase composition of the sludge roasting products at 1100 °C.

| Phase name | Chemical formula | Content, mass. % |
|-------------------------------|----------------------------------|------------------|
| Helenite | $2CaO \cdot SiO_2 \cdot Al_2O_3$ | 23,50 |
| Zinc sulfide | ZnS | 15,3 |
| Mayenite | $12CaO \cdot 7Al_2O_3$ | 6,75 |
| Zinc Oxide (Zincite) | ZnO | 9,27 |
| Larnit | $2CaO \cdot SiO_2$ | 22,07 |
| Gypsum anhydrite | $CaSO_4$ | 9,11 |
| Zinc Sulfide Oxide (Wurtzite) | $Zn(S_{0,98}O_{0,12})$ | 14,0 |

To identify C_3A formation inhibition reasons in high-sulfate clinker, raw mixtures were roasted, designed to produce typical portland cement clinker with modular characteristics of $KN=0.92$, $n=2.3$ and $p=1.69$. For the portland cement clinker preparation, the raw mix from limestone, clay, quartz sand and natural gypsum was used. During the preparation, the gypsum introduction into the mixture was calculated with following ratio: raw mix/gypsum - 95/5%. It was made to achieve more than 2 mass.% SO_3 in the mixture. The mixture was homogenized in a laboratory mill by co-grinding for 30 minutes. The homogeneous mixture was moistened and pressed at the pressure of 50 MPa. Samples were roasted at temperatures from 1100 to 1300 °C. The phase analysis data of roasted products are shown in Fig. 1. Free lime contents in the roasted products are presented in table 2.

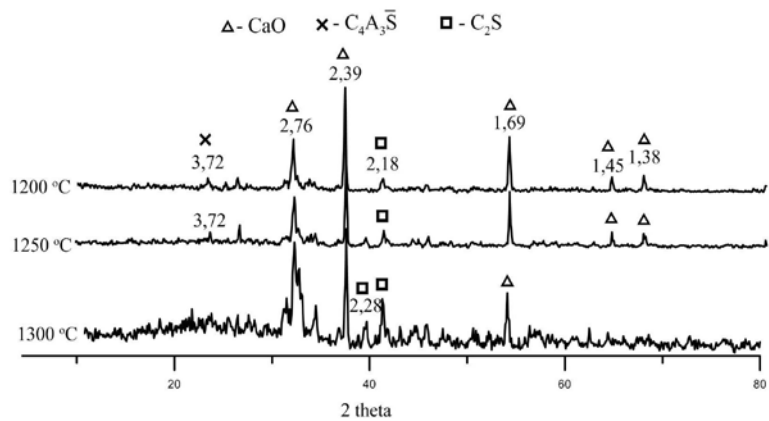


Fig. 1. The phase analysis data of roasted products.

Table 1. Free lime contents in the roasted products

| T, °C | 1100 | 1200 | 1300 |
|--------------|------|-------|------|
| CaO, mass. % | 14,0 | 13,84 | 11,6 |

Figure 1 and Table 2 indicate that the introduction of 5 mass.% gypsum into the raw mix suppresses the C_3S formation during roasting. Instead of C_3S , a significant amount of free lime are remain in the clinker. When similar clinker is heated to the temperature of 1350 °C, it is completely melted. In the melt, that heated up to 1600 °C, C_3S could be

formed during overheating over melting point, but about 6.2% of free lime will be present in the melt.

It is likely that the well-crystallized free CaO formation is responsible for the C₃S formation suppression in clinker in the presence of SO₃. This phase does not soluble in the melt, so it cannot contribute to the conversion of C₂S to C₃S. The absence of C₃S in clinker reduces its refractoriness and promotes the melt appearance at temperatures below the portland cement clinker synthesis temperature.

The formation of a free lime significant amount in clinker during the gypsum decomposition is unlikely. Since, a stoichiometric ratio of CaO and SO₃ in gypsum-anhydrite, respectively, 41.19 and 58.81 mass.%, just 2.06 mass.% free CaO may form from decomposition. But at the 1300 °C more than 11 mass.% free CaO was formed during laboratory experiments.

To clarify reasons for the free CaO significant amount appearance in a high-sulfate clinker, the thermodynamic analysis of C₃A and 4CaO·Al₂O₃·Fe₂O₃ (C₄AF) formation reactions was carried out according to [4] and the 4CaO·3Al₂O₃ (C₄A₃) formation according to [5] was carried out. Results given in the table 3.

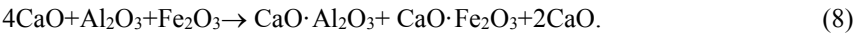
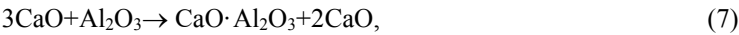
Table 2. Gibbs energy changes for C₃A and C₄AF formation with temperature rising [4,5].

| № | Reaction | ΔG°, KJ/mol, accordint to T, K | | | | |
|---|--|--------------------------------|--------|--------|--------|--------|
| | | 298 | 1023 | 1200 | 1400 | 1500 |
| 1 | 3CaO+Al ₂ O ₃ =3CaO·Al ₂ O ₃ | -17,0 | -41,8 | -47,0 | -52,9 | -55,7 |
| 2 | 4CaO+Al ₂ O ₃ +Fe ₂ O ₃ = 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ | -49,3 | -64,9 | -64,1 | -60,83 | -58,1 |
| 3 | 3CaO+3Al ₂ O ₃ +CaSO ₄ = 3CaO·3Al ₂ O ₃ ·CaSO ₄ | -99,1 | -445,1 | -583,6 | -758,9 | -853,5 |
| 4 | CaO·Al ₂ O ₃ +2CaO=3CaO·Al ₂ O ₃ | +33,7 | +32,3 | +31,7 | +33,26 | +34,4 |
| 5 | CaO·Al ₂ O ₃ +CaO+2CaO·Fe ₂ O ₃ = 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ | +10,4 | +39,7 | +49,0 | +60,3 | +66,2 |
| 6 | CaO·Al ₂ O ₃ +2CaO+CaO·Fe ₂ O ₃ = 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ | +42,45 | +72,1 | +79,77 | +79.8 | +83,7 |

According to the given data, in the absence of SO₃ in clinker, the C₃A and C₄AF synthesis is thermodynamically possible from simple minerals (CaO, Al₂O₃ and Fe₂O₃) (reactions 1-2). In the case of the SO₃presence in clinker, the reaction 3 (formation of calcium sulfoaluminate – C₃A₃CS) is thermodynamically preferable, since the Gibbs energy chage of this reaction over the entire temperature range is more negative than that of reactions 1 and 2.

There are different opinions about the mechanism of C₃A₃CS formation in clinker during heat. According to [5], the C₃A₃CS synthesis, due to an lime excess at the time of its formation, begins with the formation of mayenite (12CaO·7Al₂O₃ – C₁₂A₇) according to the scheme C₁₂A₇ → CA → C₃A₃CS. According to [6], in the pressed raw mixture, due to its higher reactivity, the C₃A₃CS synthesis proceeds according to the scheme CA₂ → CA → C₂A₂ → C₃A₃ → C₃A₃CS with the formation of calcium monoaluminate (CA) at temperatures of about 700 °C and its presence throughout the entire roasting temperature range up to 1300 °C. The C₃A and C₄AF formation is thermodynamically impossible in the CA presence (reactions 4, 5, 6).

Consequently, if the raw mix is calculated according to the usual scheme for the C₃A and C₄AF formation in high-sulfate clinker, but in fact, low-base aluminates and calcium ferrites form in high-sulfate clinker, then reactions 7 and 8 occurs instead of reactions 1 and 2 and lime remains unbound to minerals and free:



Free lime accumulates in the clinker from the temperature of calcium carbonate decomposition to the appearance of the liquid phase due to the difference in lime content in the C₃A, that used in the calculation, and the CA, that actually formed. In total, from the gypsum decomposition and the lime content difference in calcium aluminates, in clinker free lime can remains in an amount of about 5% in temperature range from calcium carbonate decomposition up to the liquid phase appearance. This amount is sufficient to suppress the C₃S formation at the moment of the appearance of liquid phases.

Since in the presence of SO₃ only C₂S formed in the clinker and C₃S is absent, due to the lime content difference in these minerals, the total free lime content reaches 11 mass.% at synthesis completion temperatures. With an increase in the temperature of the melt up to 1600 °C, C₃S is formed in an insignificant amount, but free CaO does not dissolve and remains in an amount of about 6 mass.%.

Taking into account the high-sulfate raw material mixtures test results, a method was developed for calculating the raw mixture composition containing gypsum-anhydrite, which allows C₃S significant amount forming in portland cement clinker. This technique was used in calculating the raw material mixture composition based on sludge from the production of synthetic fibers to form portland cement clinker typical phases in it. The data of roasted products phase analysis are presented in fig. 2

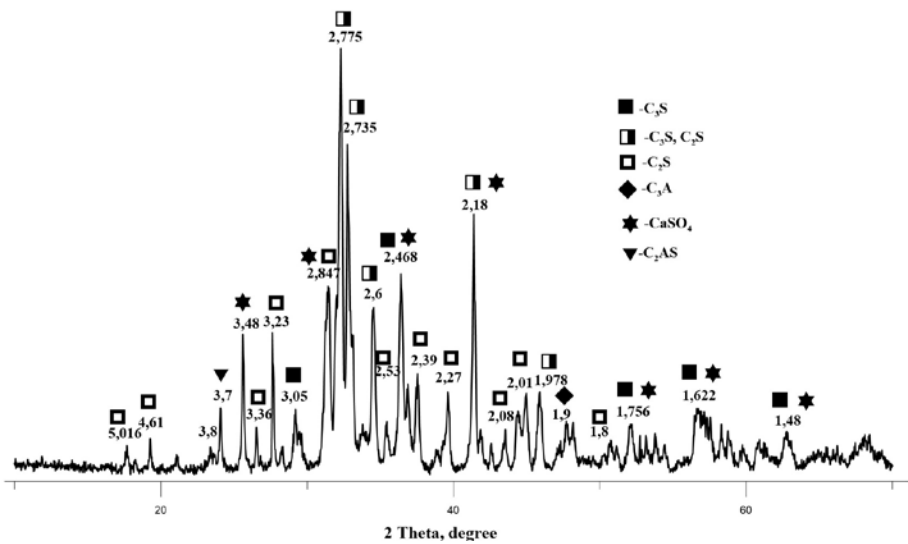


Fig. 2. Phase composition of roasted products.

The phase analysis data show that it is possible to form typical phases of Portland cement clinker in roasted products. There are also gypsum anhydrite remains. Checking the obtained clinker setting time showed that it has normal setting times that meet the regulatory documents requirements.

The reported study was funded by RFBR according to the research project № 18-29-24064\18.

References

1. J.I. Bhatti, *Role of Minor Elements in Cement Manufacture and Use* (Portland Cement Association, Skokie, Illinois, 1995)
2. H. Sayed, R. Ltief, T. Rizk, *Influence of the clinker SO_3 on the cement characteristics*, Cement And Concrete Research **41**, pp. 913-919 (2011).
3. H. Sayed, R. Ltief, T. Rizk, *Calculation of the C_3A Percentage in High Sulfur Clinker*, International Journal of Analytical Chemistry, **Vol. 2010**, 5 pages (2010) Article ID 102146
4. V.I. Babushkin, G.M. Matveev, O.M. Mchedlov-Petrosyan, *Thermodynamics of silicates* (Moscow, Stroiizdat, 1986)
5. T.V. Kuznetsova, *Aluminate and sulfoaluminate cements* (Moscow, Stroiizdat, 1986)
6. M.A. Mikheenkoy *Influence of raw mix pressing on the reduction of energy consumption in the production of cement*, ALITinform., **№ 2.**, p. 50-57 (2011)